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REPORT ON POLLUTION OF THE MERRIMACK RIVER AND CERTAIN TRIBUTARIES

PART IV. PILOT PLANT STUDY OF BENTHAL OXYGEN DEMAND

FEDERAL WATER POLLUTION CONTROL ADMINISTRATION
BOSTON, MASSACHUSETTS

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PART IV -- PILOT PLANT STUDY OF BENTHIC OXYGEN DEMAND

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TABLE OF CONTENTS

	Page No.
INTRODUCTION	1
MATERIALS AND METHODS	2
Description and Operation of the Pilot Plant	2
Water Supply and Sediments	3
Chemical Analyses	6
Computations	6
EXPERIMENTAL RESULTS	9
DISCUSSION	10
SUMMARY	13
CONCLUSIONS	13
REFERENCES	14

LIST OF FIGURES

Figure No.		Follows Page No.
1	Pilot Plant Schematic.	2
2	Areal Oxygen Demand of Recent and Aged Benthic Sediments of 1.5 cm Depth	9
3	Areal Oxygen Demand of Aged Benthic Sediments. . . .	9
4	Calculated L_{d_o} versus Sediment Depth	9
5	Cumulative Areal Oxygen Demand	9
6	Comparison of Calculated and Observed Values of L_d with Recent Sediment of 1.5 cm Depth	9
7	Comparison of Calculated and Observed Values of L_d with Aged Sediment of 1.5 cm Depth	9
8	Comparison of Calculated and Observed Values of L_d with Aged Sediment of 10 cm Depth.	9
9	Comparison of Calculated and Observed Values of L_d with Aged Sediment of 15 cm Depth.	9
10	Comparison of Calculated and Observed Values of L_d with Aged Sediment of 20 cm Depth.	9
11	Variation of k_4 with Sediment Depth.	9
12	Effect of Nitrification on Oxygen Demand Rate with Recent Sediment of 1.5 cm Depth.	9
13	Effect of Nitrification on Oxygen Demand Rate with Aged Sediment of 1.5 cm Depth.	9

LIST OF TABLES

Table No.		Page No.
1	Sediment Type, Depth, and Volume at Start-up of Pilot Plant.	4
2	Chemical and Biochemical Analyses of Sediments at Start of Pilot Plant Run.	5

INTRODUCTION

An estimate of the oxygen demand of the sediments which accumulate in stream beds is a practical necessity to the engineer engaged in the interpretation of oxygen levels in stream pollution surveys. Evaluating this variable is a difficult task. Different empirical approaches for estimating the sediment oxygen demand have been reported [1] [2]. Recently, a benthic respirometer has been developed [3] to measure oxygen levels over the sediments in situ.

In this study, a pilot plant was erected to operate under controlled laboratory conditions using bottom sediments taken from different sites in the Merrimack River bed downstream of certain municipal sewer outfalls. The sediments studied in the pilot plant include those solids which normally would be removed in a primary settling device receiving raw municipal sewage. The method outlined herein considered the variability of the rate of biochemical assimilation of the residues and formulates the findings in terms of the benthic equation of Camp [4]. In addition, the effect of sediment depth on the areal oxygen demand of these sediments was studied.

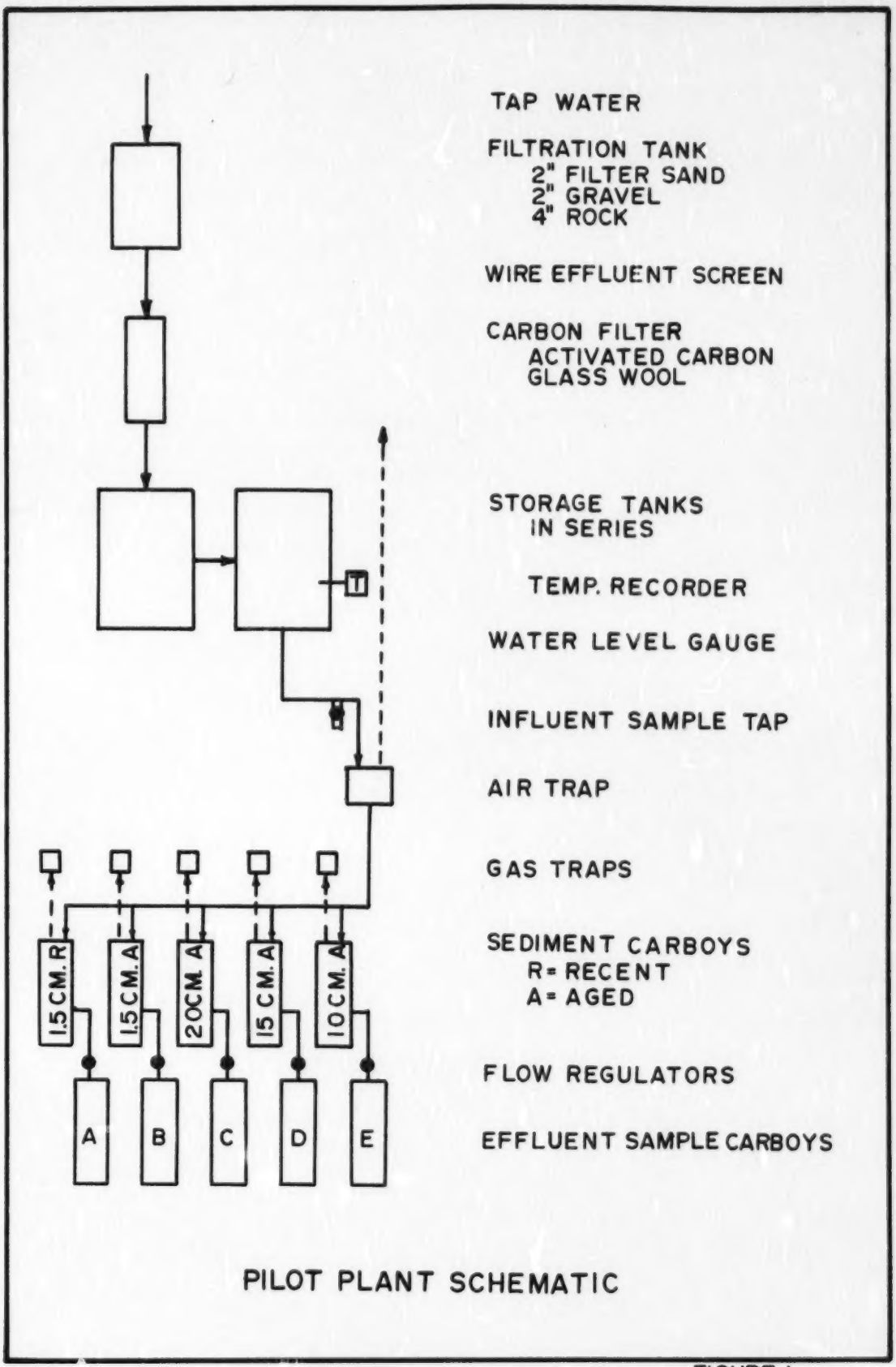
MATERIALS AND METHODS

Description and Operation of the Pilot Plant

The basic elements of the pilot plant used in this study were a carbon filter (for chlorine removal), a sand filtration tank, galvanized iron water storage drums, a series of five 20-liter glass carboys containing the sediments, and five additional carboys to receive the effluent. These elements were connected by means of glass and plastic tubing. A schematic diagram of the pilot plant is given in Figure 1.

After passing through the sand and carbon filters, water entered the storage drums (which were filled every day) and equilibrated at room temperature (20-25°C). This is also the normal summer temperature in the river from which the samples were taken. Temperature of the water in the drums was determined by a recording thermometer. From the storage drums water flowed continuously through a manifold into the five sediment carboys and from there discharged into the effluent carboys.

The flow rate from each carboy was individually regulated twice a day by means of screw clamps on rubber tubing. The rate was set at approximately 20 liters per day. The effluent volume was determined each 24-hour period by measuring the height of water in the effluent carboy with a yardstick. The actual volume was then taken off a calibration graph relating fluid height and volume.



PILOT PLANT SCHEMATIC

FIGURE 1

Decomposition gases were removed through gas traps which were held above the water level in the storage tanks. Gases from the carboy with 10 cm of sediment were analyzed after being measured in a Harvard manometer in order to check for the presence or absence of anaerobic conditions.

Water Supply and Sediments

Tap water used in this study originated from the Merrimack River. Raw river water was treated at the Lawrence, Massachusetts, municipal plant by alum flocculation, activated carbon, sand filtration, aeration, and chlorination.

Two types of sediments from the Merrimack River were used. Although they are physically and chemically characterized as shown in Tables 1 and 2, arbitrary terms of "recent" and "aged" were selected to more generally define them. Ideally, these sediments could be further characterized in terms of their percent solids of sewage or non-sewage origin following a method such as the organic analyses performed by Heukelekian (5). The "recent" deposit was taken 100 yards downstream of a large outfall and was assumed to consist largely of the municipal sewage sediments discharged to the river. The "aged" sediments were taken several miles downstream and represented deposits in a more advanced stage of decomposition. Since the rate of diffusion of oxidizable substances into the supernatant water, rather than simply the sludge depth, is believed to control the rate of oxygen demand of the sediment, no attempt was made in the field to collect undisturbed sediment samples from different depths. Layering or sediment depths are transient states affected by many variables such as stream

hydraulics, and any reproduction in the laboratory of these layers of sediments did not seem justified within the scope of this study.

Both sediments were mixed by impeller motor and by hand prior to being poured into the carboys. The sediment type, along with the depth and volume of deposits in the carboys, is given in Table 1. Physical and chemical analyses of each sediment type were carried out at the beginning of the study. These data are summarized in Table 2.

TABLE 1

SEDIMENT TYPE, DEPTH, AND VOLUME
AT START-UP OF PILOT PLANT

Carboy	Sediment Type	Depth (cm)	Volume (ml)
A	recent	1.5	1,180
B	aged	1.5	1,180
C	aged	20	11,940
D	aged	15	8,950
E	aged	10	5,970

TABLE 2

CHEMICAL AND BIOCHEMICAL ANALYSES OF SEDIMENTS AT START OF PILOT PLANT RUN

Sediment	pH	% Moisture	Specific Gravity	Residue, gms/50 ml		
				Total	Volatile	Fixed
recent	6.6	40.5	1.61	47.70	1.14	46.56
aged	6.8	37.5	1.63	50.75	1.40	49.35

Sediment	Total Fe mg/g Fixed Solids	NH_3-N mg/g Total Solids	ORG-N mg/g Total Solids	Total Mn mg/g Fixed Solids
recent	2.20	0.02	3.30	0.01
aged	3.04	0	0.86	0.01

Sediment	t, days:	Biochemical Oxygen Demand*, mg O_2/g Volatile Solids			
		t = 2	t = 5	t = 10	t = 15
recent		73.7	174	234	248
aged		20.4	44.7	74.8	86.7

NOTE: *This test was carried out by the dilution method given in Standard Methods (Eleventh Edition), Part IV. The DO determinations were made using the Winkler Method--azide modification.

Chemical Analyses

Chemical analyses routinely employed in this study were: dissolved oxygen (azide modification of Winkler method), nitrite, nitrate (phenol-disulfonic acid method), ammonia (distillation procedure), organic nitrogen, and ferrous and total iron (o-phenanthroline method).

Dissolved oxygen determinations were performed daily on the effluent from the storage tanks and the effluent of each of the five sediment carboys. Analyses for nitrite, nitrate, ammonia, organic nitrogen, and ferrous and total iron were performed on 3- to 7-day composited samples after acidification and storage at 10°C.

All methods and procedures used conformed to those listed in Standard Methods, Eleventh Edition (6).

Computations

To determine the sediment volume and to compute the surface area of the sediments, it was necessary to know the inside radius of the glass carboys. This was determined by measuring the volume of water necessary to bring the fluid level to a specific height. Solving for r in the formula of a cylinder ($V = \pi r^2 h$) gave a value of r = 13.8 cm and a surface area equal to 0.0596 square meters. A correction factor in the sediment volume determination was made for a slight irregularity in the bottom of the carboy. The daily areal oxygen demand (DAOD) was computed by using the following formula:

$$DAOD = V_e (DO_i - DO_e) \frac{1}{1000\ A} \quad \ldots\ldots\ldots\ldots 1$$

where:

DAOD = daily areal oxygen demand, gms $O_2/m^2/day$

V_e = daily carboy effluent volume, liters/day

DO_i = dissolved oxygen of carboy influent, mg/liter

DO_e = dissolved oxygen of carboy effluent, mg/liter

A = surface area of deposit, 0.0596 square meters

Camp's benthic equation [4] includes the term L_{d_o} which is defined as the initial areal BOD of the bottom deposits at the start of decomposition. This definition implies that L_{d_o} is similar to the ultimate carbonaceous oxygen demand term L in the familiar BOD equation $y = L\ (1-10^{-kt})$.

Using BOD data from Table 2, the rate constant was obtained by Thomas's [7] graphical method. After solving for L in the BOD equation, and knowing the amount of the initial volatile solids and the volume and surface area of the deposit, the initial ultimate areal oxygen demand L_{d_o} is obtained.

$$L_{d_o} = (IVS)\ (V_s)\ (L)\ \frac{1}{1000\ A} \quad \ldots\ldots\ldots\ldots 2$$

where:

L_{d_o} = initial ultimate areal oxygen demand, gm/m^2

IVS = initial volatile solids of the sediment, gm/ml

V_s = volume of sludge added to the carboy, ml

L = ultimate oxygen demand, mg/gm IVS

A = surface area of deposit = 0.0596 m^2

Evaluation of the term L_d, the total areal BOD of the bottom deposits in Camp's equation

$$L_d = L_{d_o} \cdot 10^{-k_4 t} \quad \ldots\ldots\ldots\ldots\ldots 3$$

requires not only the value of the L_{d_o} but also the value of the areal demand rate constant, k_4.

Values of k_4 for the various sediment depths were determined as the slope b of the line, $\log y = \log a + bx$ where y values were L_d values obtained by pilot plant and x values were days after start-up of the operation.

Experimental values of L_d were obtained as the difference between the initial ultimate areal BOD, L_{d_o}, and the cumulative areal oxygen demand (L_c). This may be expressed as:

$$\text{Experimental } L_d = L_{d_o} - L_c \quad \ldots\ldots\ldots\ldots 4$$

Finally, values of L_d calculated from Camp's equation and experimental values of L_d obtained by pilot plant were plotted.

EXPERIMENTAL RESULTS

The daily areal oxygen demands of the "recent" and "aged" deposits at 1.5 cm versus time are shown in Figure 2, while similar data for the "aged" sediments are presented in Figure 3. Flocculated material (probably alum) in the storage drums was noted after 50 days. The pilot plant operation was interrupted and the drums were cleaned.

A graph relating the values of the initial ultimate areal oxygen demand with sediment depth is presented in Figure 4. Thus, if all the sediments of the same type would be completely oxidized, the oxygen demand would be directly proportional to depth. Cumulative areal oxygen demands for the five tests are indicated on Figure 5.

Comparisons of the calculated areal oxygen demand at different times, using the value of k_4 obtained from the slope of the line of best fit on a semi-log graph, with the observed results are presented in Figures 6 through 10. These graphs show any deviations from the normal pattern. The variation of k_4 values with sediment depth is given in Figure 11.

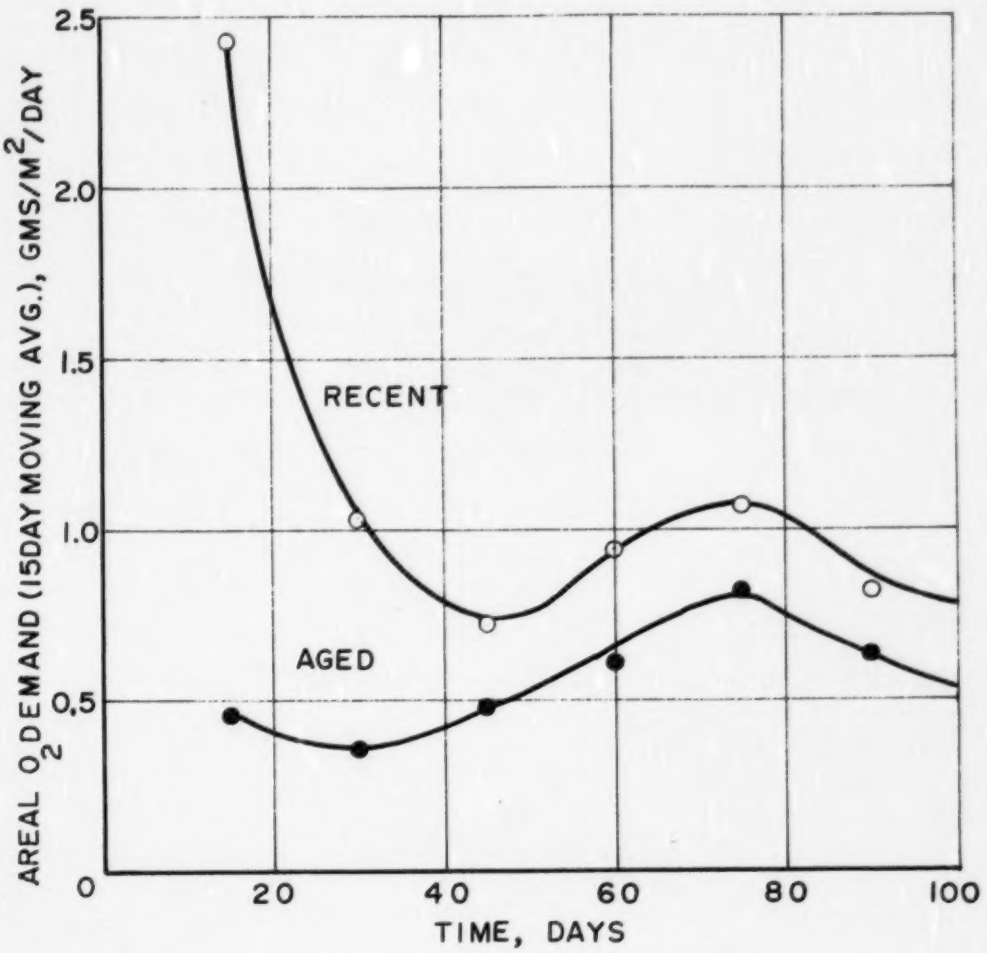
Part of the oxygen demand attributed to the sediments was thought to result from the oxidation of nitrogenous compounds. Graphs of the calculated oxygen demand derived from the oxidation of ammonia to nitrate are presented in Figures 12 and 13, along with the observed daily oxygen demand of the sediments. The nitrate-nitrogen oxygen equivalents were based on the difference in nitrate-nitrogen values obtained on the influent control water and the effluent. The chemical analyses were carried out on composited samples. The observed oxygen demands are based on averages of the daily demand for the same time period.

DISCUSSION

The graphs of the daily areal oxygen demand in Figure 2 indicate that, except for the initial phase in the recent deposit, both of the 1.5 cm sediments followed a roughly parallel course, increasing in oxygen demand up to 75 days and then tapering off. The recent deposit consistently showed a daily demand of about 0.25 $gm/m^2/day$ higher than the aged sediment. The daily areal oxygen demands of the deeper sediments in Figure 3 show some fluctuations but tend to remain in the fairly narrow range of 0.7-1.0 $gm/m^2/day$. There was practically no difference in areal oxygen demand in the 15 and 20 cm depths.

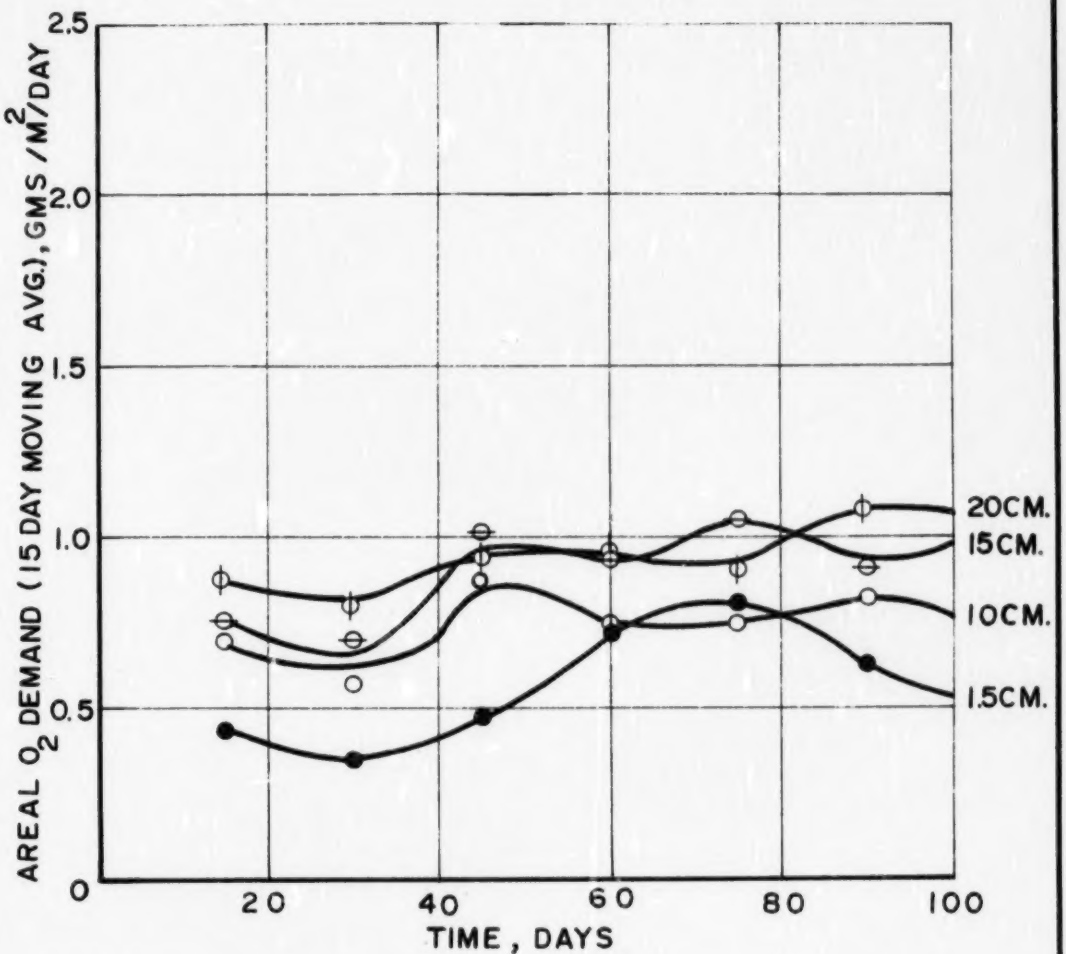
One factor influencing the observed fluctuations in daily oxygen consumption could have been the oxidation of nitrogenous materials. When the oxygen demand believed to have resulted from nitrification was plotted along with the observed oxygen demand (Figures 12 and 13), there was a definite correlation in the location and magnitude of the peaks. In the two shallow deposits, the nitrate-nitrogen oxygen equivalent approached nearly 37 to 44 percent of the total areal oxygen demand at the maximum. Both of these maximums occurred 70 to 80 days after start-up of the tests.

Although nitrification appeared to play an important role in the areal oxygen demand of the shallow sediments, it did not appear to be significant in the deeper sediments. For example, the nitrate-nitrogen oxygen equivalent reached a maximum value of 5 percent of the total areal oxygen demand in the 10 cm depth.



AREAL O_2 DEMAND OF RECENT AND AGED BENTHIC SEDIMENTS OF 1.5cm DEPTH

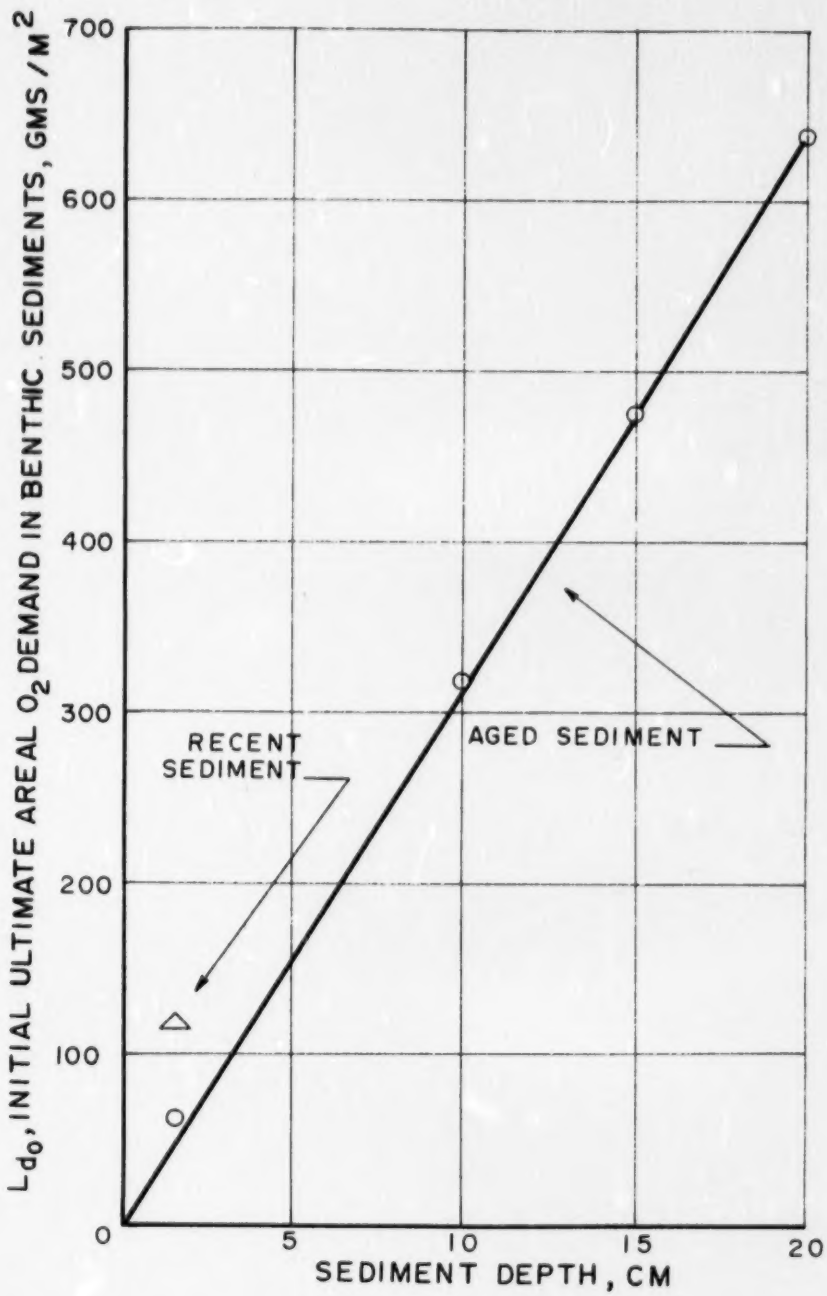
FIGURE 2



AREAL O_2 DEMAND OF AGED

BENTHIC SEDIMENTS

FIGURE 3



CALCULATED L_{d_o} VS. SEDIMENT DEPTH

FIGURE 4

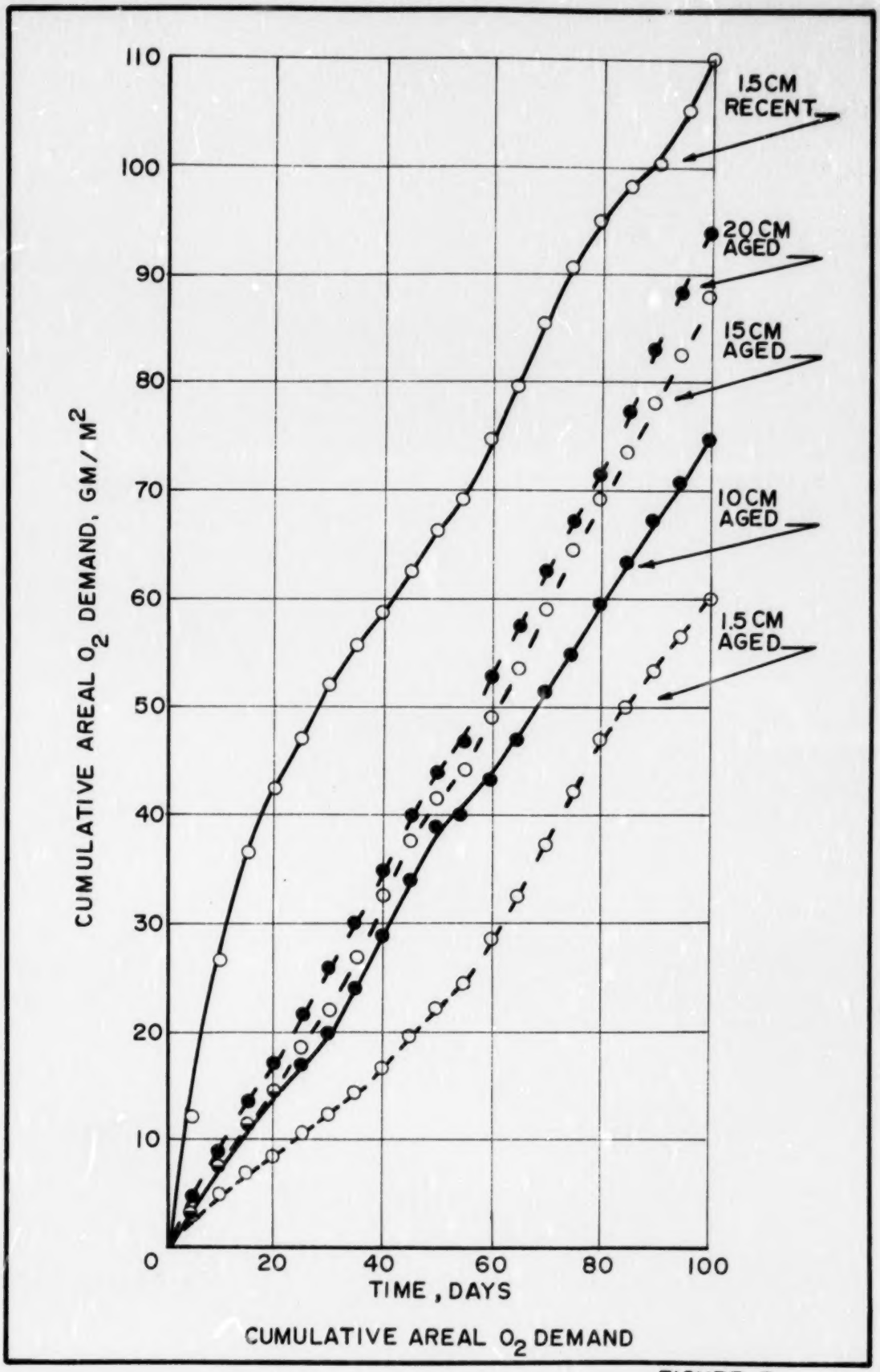
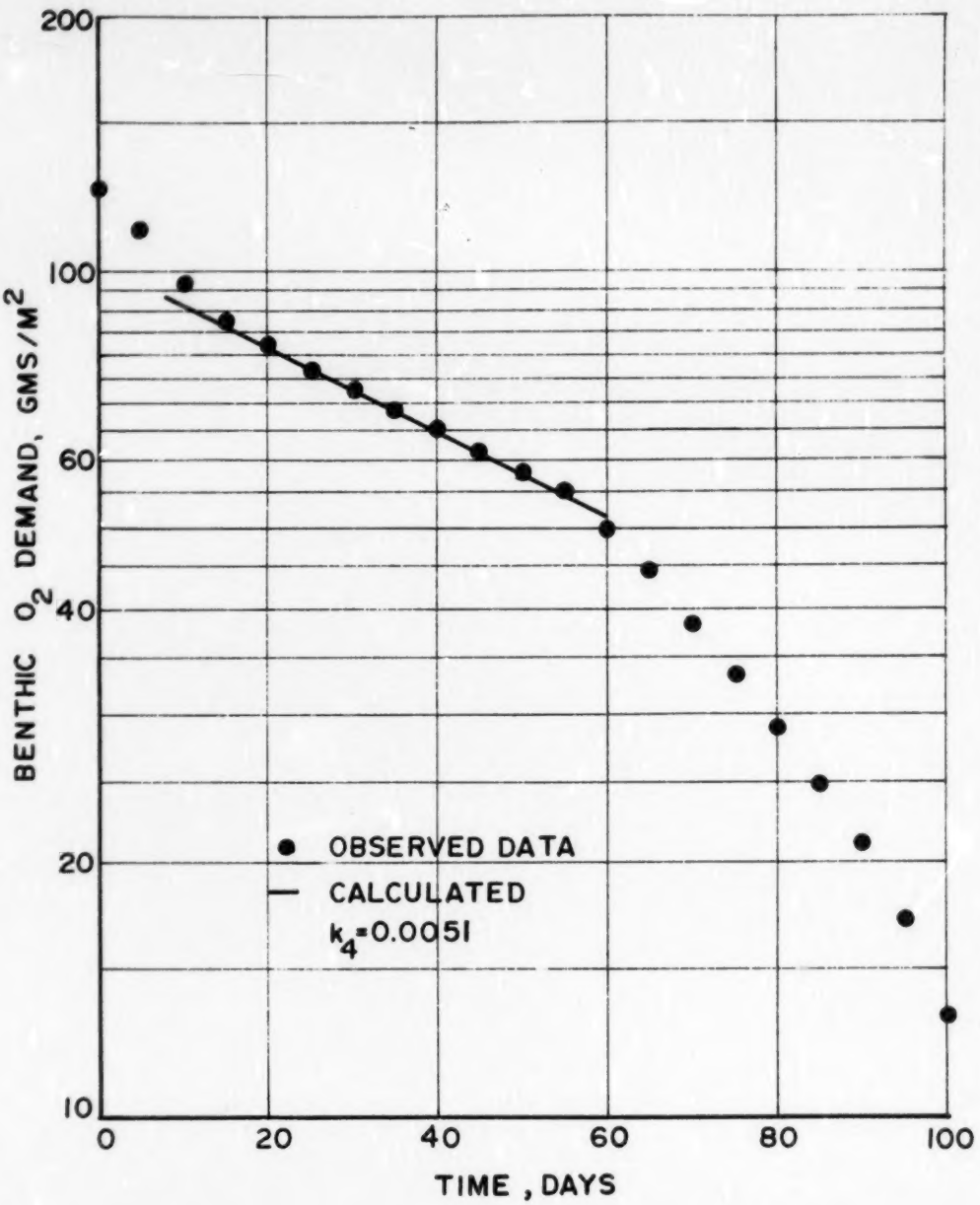
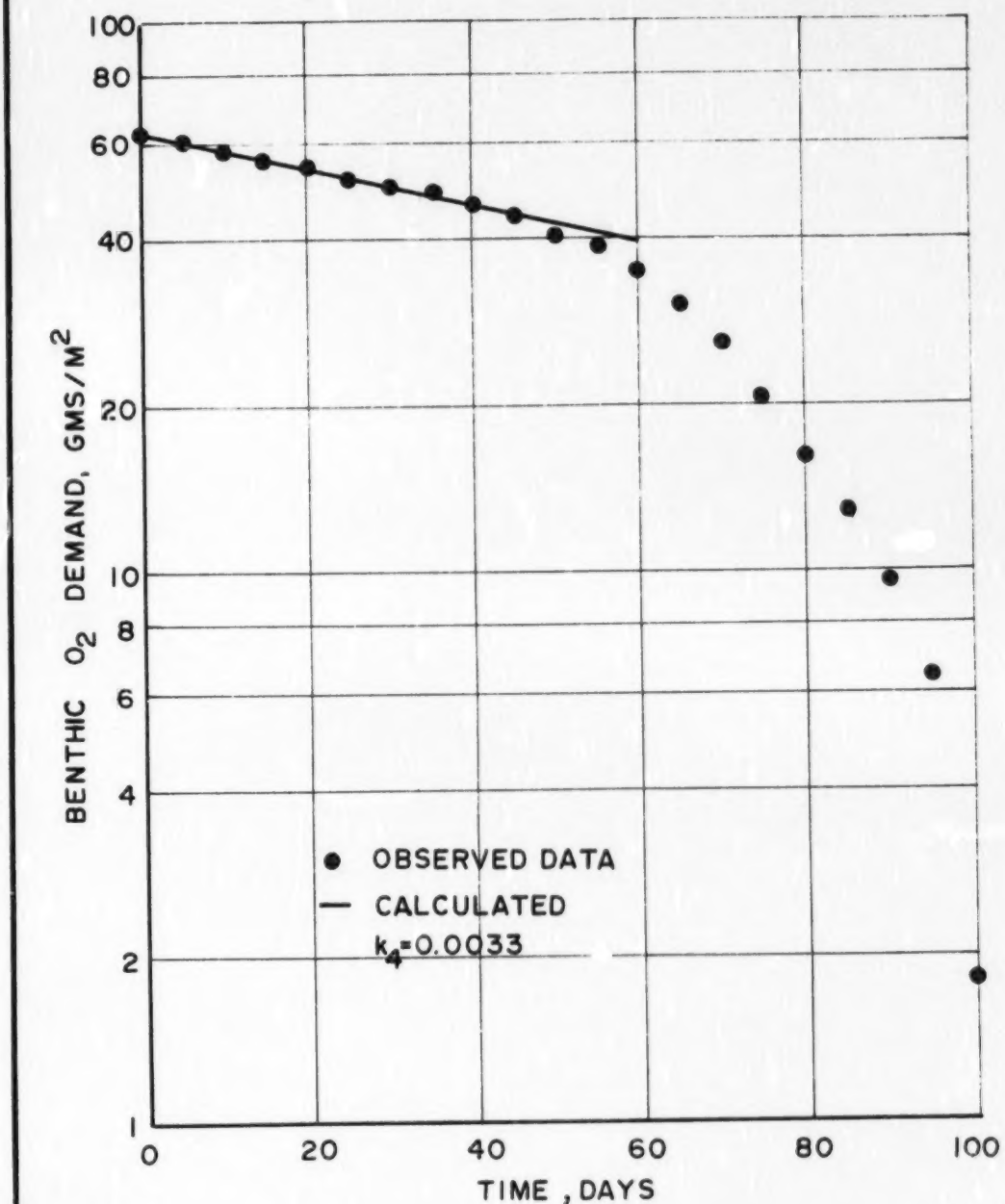

110
100
90
80
70
60
50
40
30
20
10
0
20
40
60
80
100
TIME, DAYS
CUMULATIVE AREAL O_2 DEMAND, GM/ M^2
1.5 CM RECENT
2.0 CM AGED
1.5 CM AGED
1.0 CM AGED
1.5 CM AGED
CUMULATIVE AREAL O_2 DEMAND

FIGURE 5



COMPARISON OF CALCULATED AND OBSERVED VALUES OF L_d 1.5cm RECENT SEDIMENT

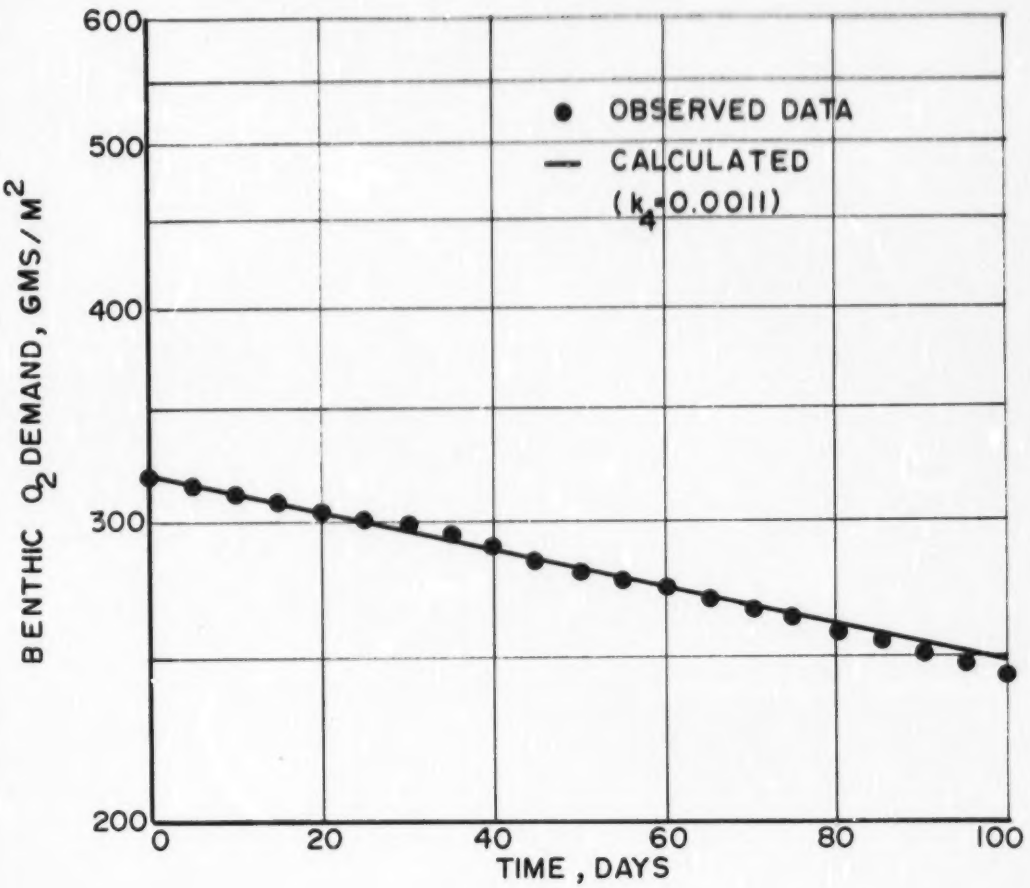
FIGURE 6



COMPARISON OF CALCULATED
AND
OBSERVED VALUES OF L_d

1.5 CM AGED SEDIMENT

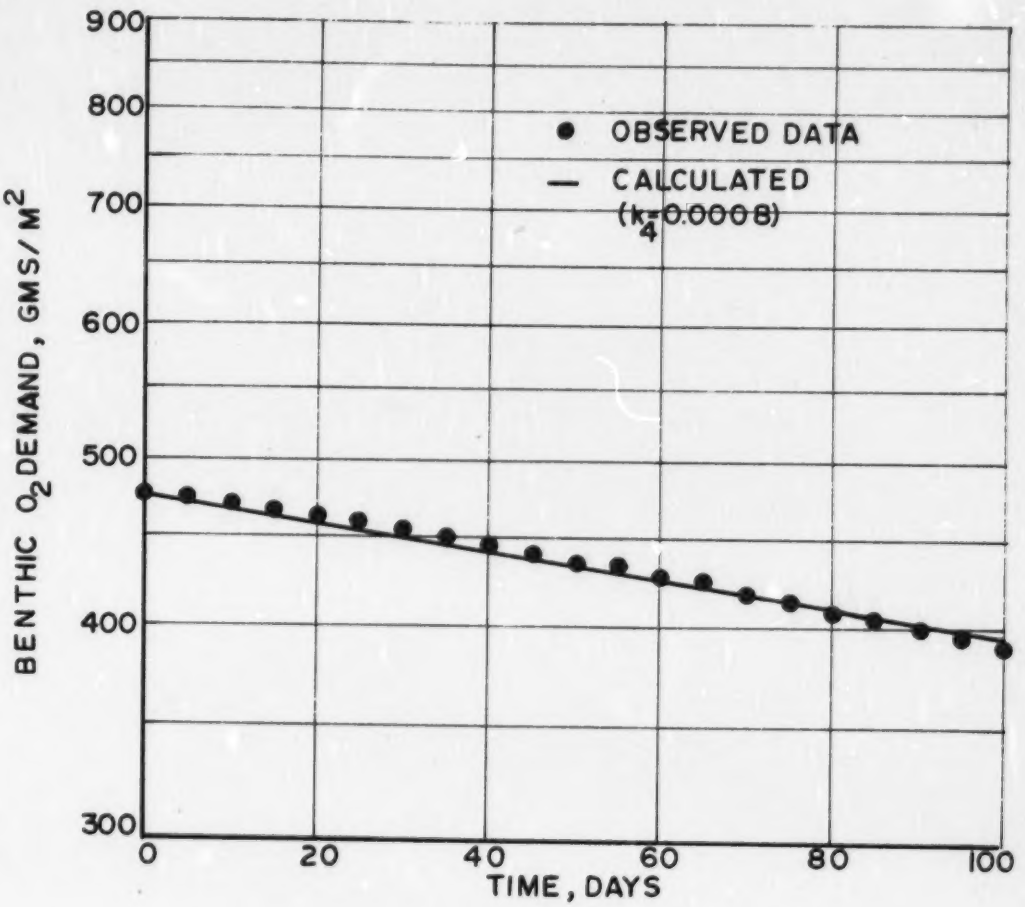
FIGURE 7



COMPARISON OF CALCULATED
AND
OBSERVED VALUES OF L_d

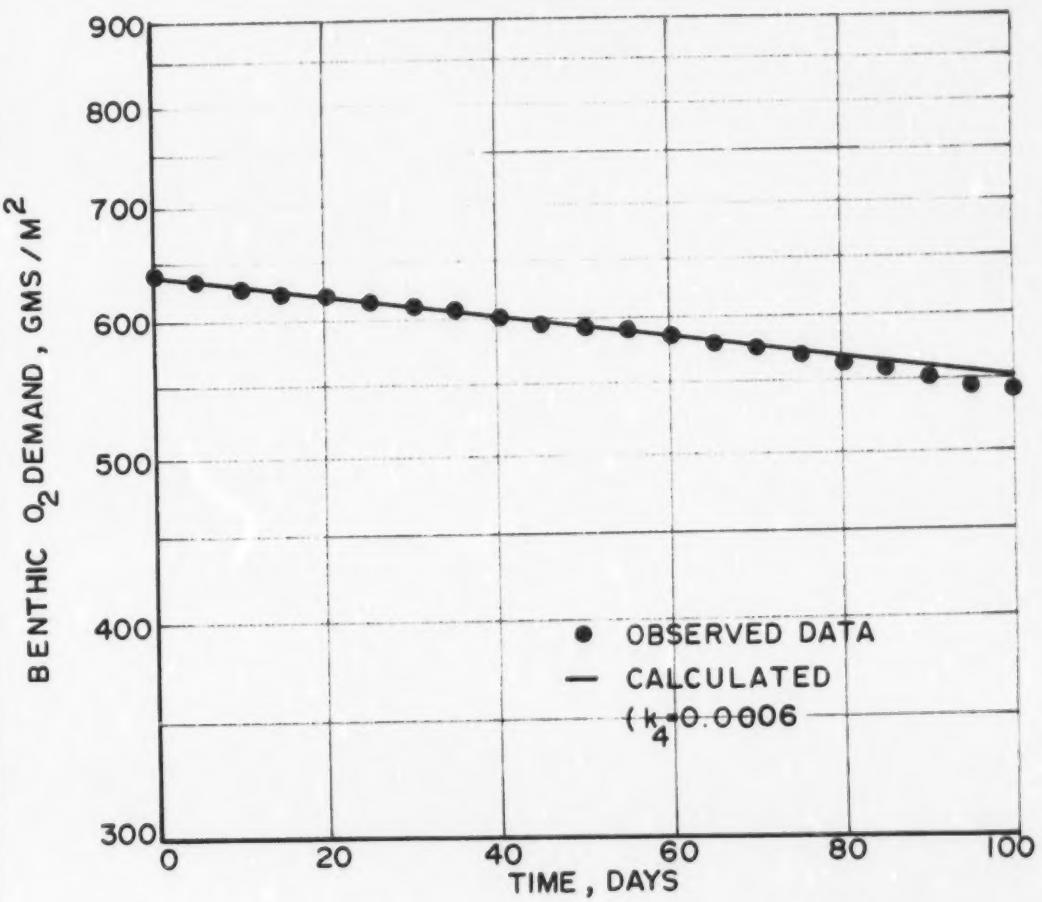
10 CM AGED SEDIMENT

FIGURE 8



COMPARISON OF CALCULATED
AND
OBSERVED VALUES OF L_d
15 CM AGED SEDIMENT

FIGURE 9



COMPARISON OF CALCULATED
AND
OBSERVED VALUES OF L_d

20 CM AGED SEDIMENT

FIGURE 10

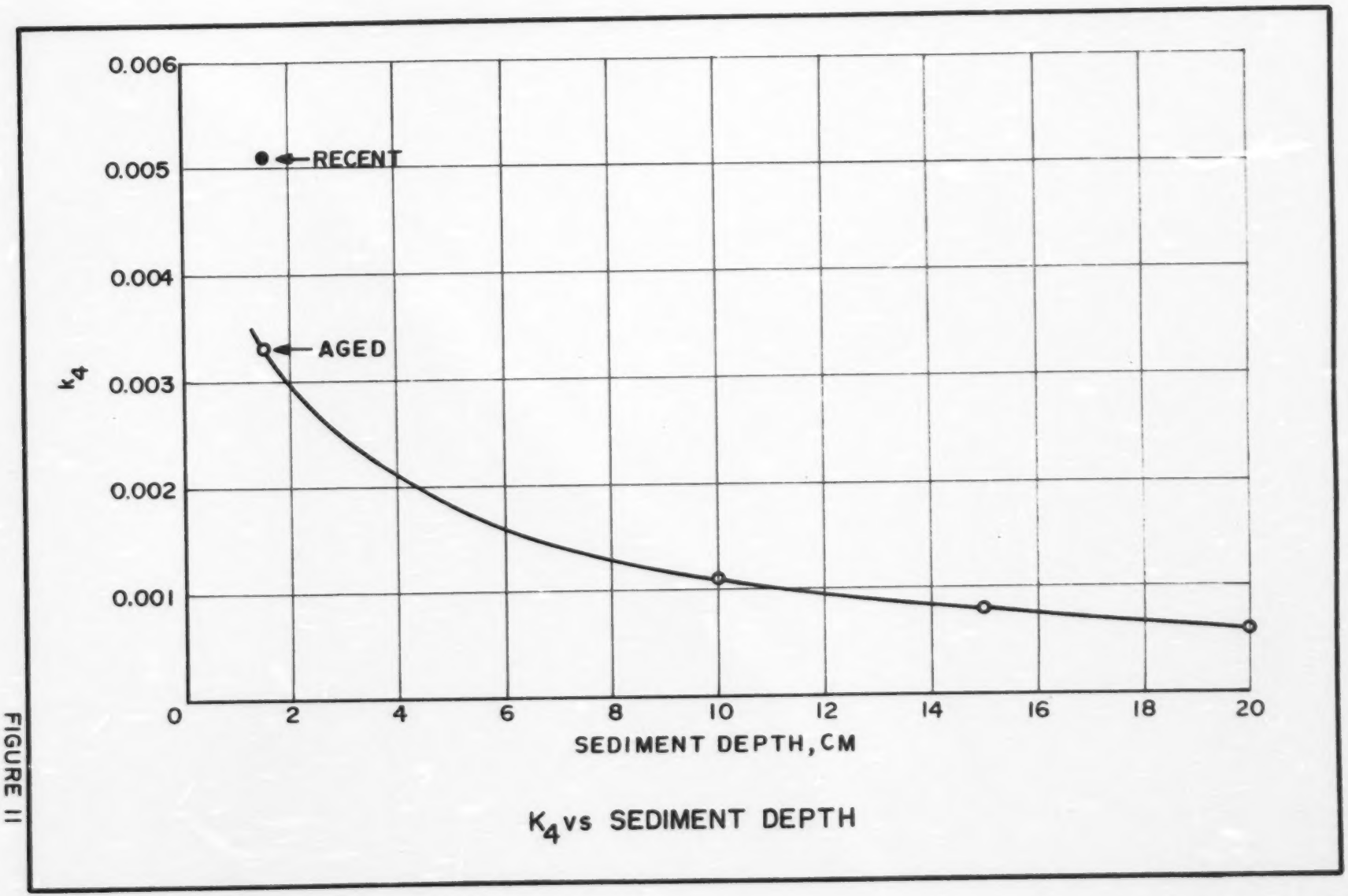
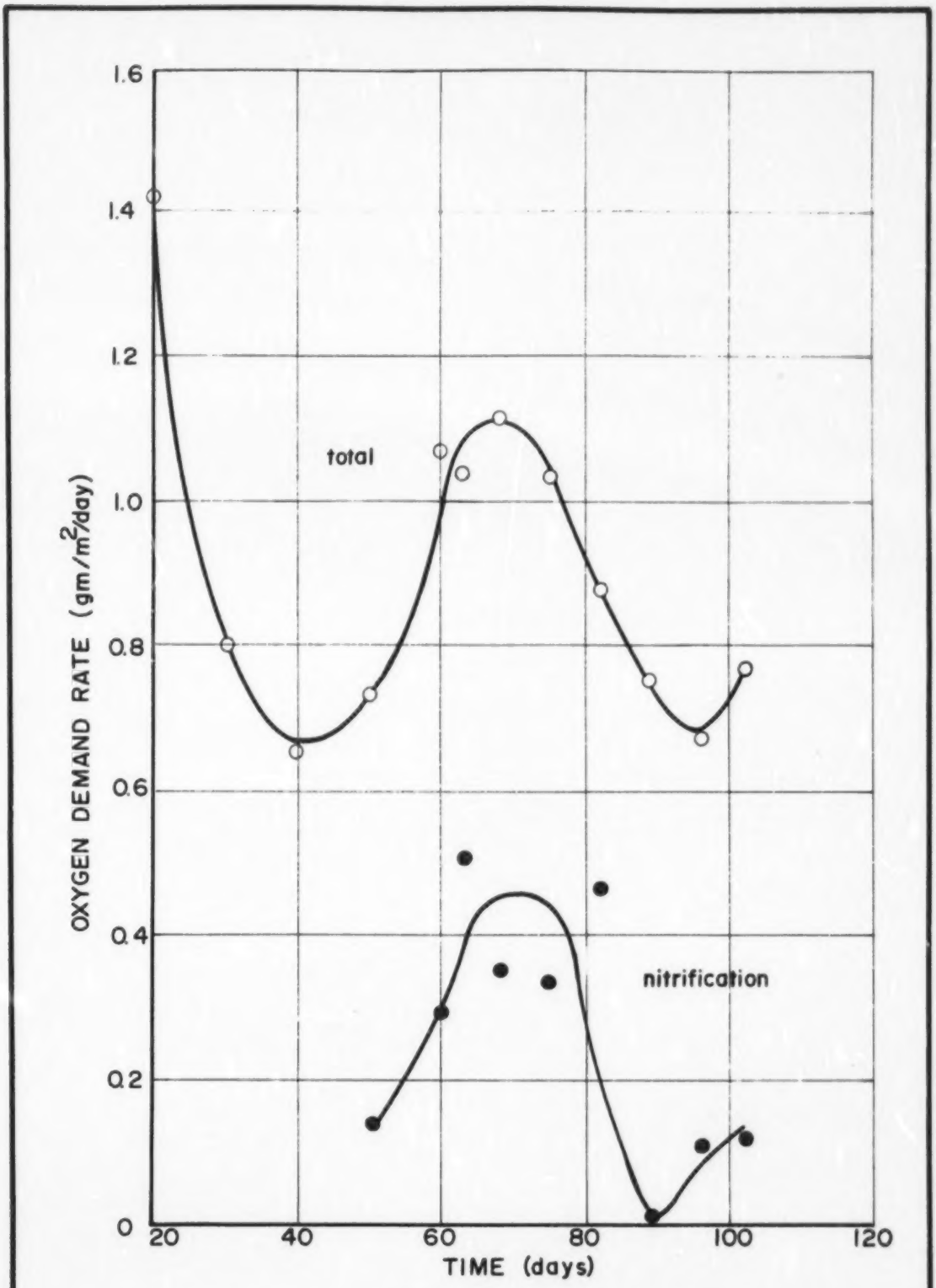


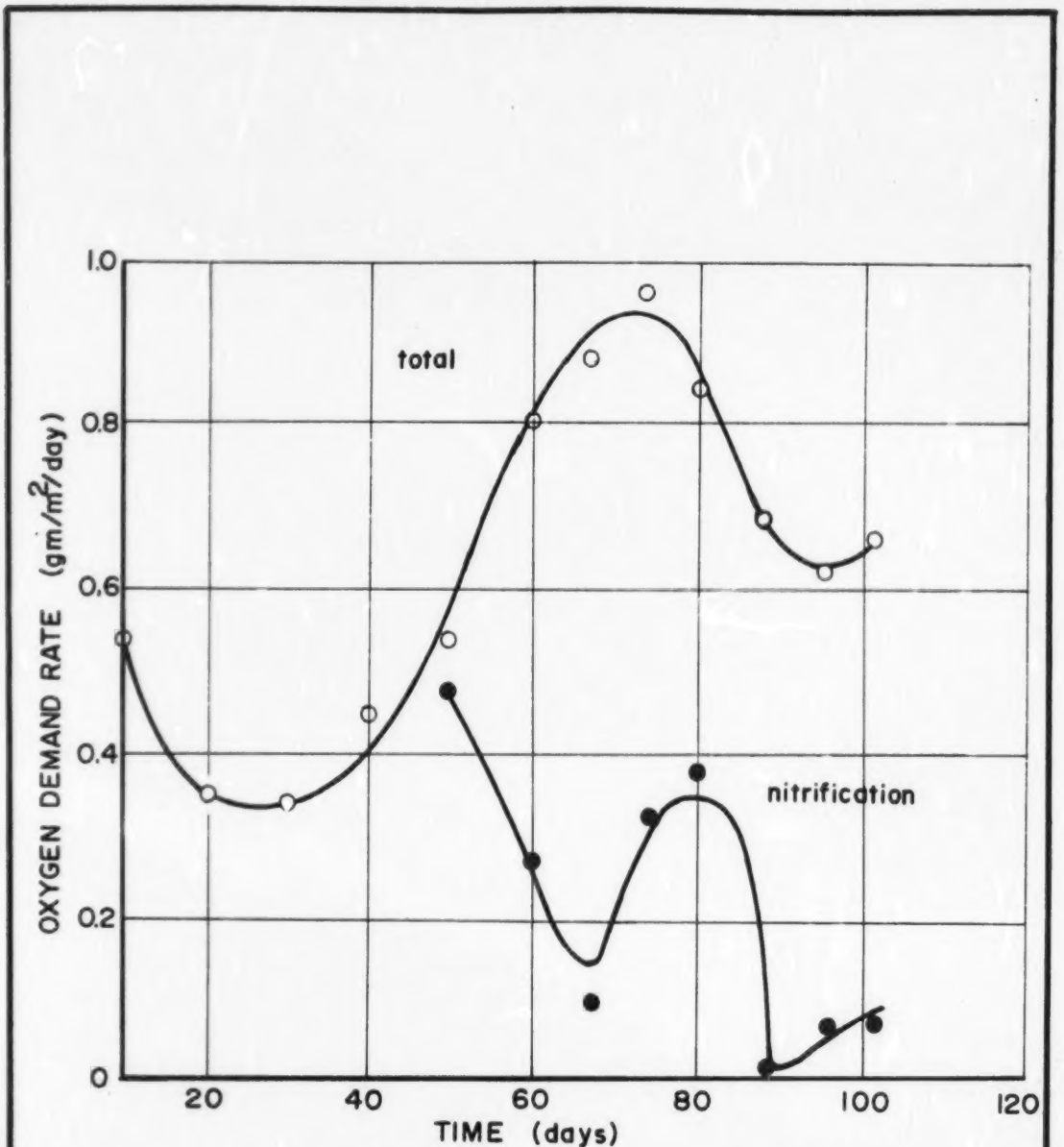
FIGURE 11

K_4 vs SEDIMENT DEPTH



EFFECT OF NITRIFICATION ON OXYGEN DEMAND RATE OF 1.5cm RECENT SEDIMENT

FIGURE 12



EFFECT OF NITRIFICATION ON OXYGEN DEMAND RATE OF 1.5 cm AGED SEDIMENT

FIGURE 13

Periodic release of gases of anaerobic decomposition from the deeper sediments indicated a reducing environment. This was confirmed by analysis of gases from the 10 cm sediment depth. These gases may have moderated nitrification to the extent shown in the minor fluctuations of the areal oxygen demand rate in Figure 3.

The plot of the cumulative areal oxygen demand of the aged deposits (Figure 5) shows that there is a fairly marked increase in demand with sediment depth.

Consideration of Figures 6 through 10 indicates that in the deeper sediments (10 to 20 cm) the benthic oxygen demand L_d as calculated from the benthic equation closely approximates the experimental values of L_d throughout the test period.

In the 1.5 cm "recent" sediment, the benthic equation closely approximates the benthal demand obtained only between 15 and 55 days. For the first 15 days, the high values of L_d may have been due to the oxidation of readily biodegradable sewage solids prior to the development of benthic conditions. After 55 days, nitrification may have been the cause of the increasing rate of demand (Figure 12).

In the 1.5 cm "aged" deposit, the benthic equation closely approximates the benthic demand obtained in the pilot plant only for the first 40 days after which nitrification may have been the cause of the increasing rate of demand (Figure 13).

SUMMARY

The areal oxygen demand of bottom sediments taken from the Merrimack River in Massachusetts was determined by a small pilot plant similar in design to that of Fair et al [8]. Parameters in the benthic rate equation of Camp [4] were evaluated on the basis of the data obtained, and the effect of sediment depth on the benthic rate constant k_4 was studied. Chemical analyses of the influent and effluent water were carried out. The effect of nitrification on the oxygen demand is discussed.

CONCLUSIONS

1. The value of the benthic rate constant k_4 varies with the age and depth of the deposit.
2. A marked decrease of k_4 with increase in sediment depth occurred between 1.5 and 10 cm. Above 15 cm no significant decrease in k_4 was observed.
3. Only the upper 15 cm of sediment had any significant effect on the areal oxygen demand.
4. The observed data were closely approximated by the equation $L_d = L_{d_o} 10^{-k_4 t}$ at all sediment depths except the 1.5 cm depth.
5. Nitrification was believed to play a role in the oxygen demand of the sediments and was especially significant in the shallow depths studied.

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